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METHODS FOR CALCULATING THE BULK MODULUS IN COMPOSITION RANGES WITH NONUNIFORM AND UNIFORM STRUCTURE

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Methods for calculating the bulk modulus of glasses with homogeneous and heterogeneous structures are proposed within a model that takes account of the different degrees of interaction between structural elements comprising two-component glasses. Lead-silicate and lead-borate glasses are studied as examples of the application of these computational methods.

Key words: two-component glasses, bulk modulus, computational methods, homogeneous and heterogeneous structures.

The existing methods of determining the elastic properties of solids by measuring the ultrasonic wave velocities (longitudinal and transverse) presuppose uniformity of the medium in which the waves propagate, i.e., all parameters which are measured are constant: the density of the wave-propagation medium, wave velocity, and elastic properties. For a heterogeneous structure the measured value of the wave velocity is a result of averaging, whose algorithm is unknown, as is whether or not the characteristics are averaged according to the same algorithm as the velocities. Thus, the application of this method to glass with heterogeneous structure is fraught with possible errors associated with incorrect application of the measured parameters — density, sound velocity — if the sizes δ of the nonuniformities are comparable to the wave length λ and completely justified if $\lambda \gg \delta$.

In the present work a method is proposed for calculating the elastic properties of glasses with a nonuniform structure on the basis of data on a property of glasses whose composition corresponds to the limits of this range, i.e., it corresponds to uniform structures.

We shall study two-component glasses with a nonuniform structure and different contents A and B of the glass former and modifier, respectively, in glass compositions of the type $xB - (1 - x)A$, where x is the molar fraction of the modifier with $0 \leq x \leq x_1$ and x_1 is the limit of the composition range for glass with nonuniform structure. As proposed in [1, 2], in this range the phases with constant composition be-

have as structural elements (SE) whose properties are independent of the composition. The glass former A is denoted as SE1, and the other structural element SE2 is the phase whose composition is $x_1 B - (1 - x_1)A$.

Since the nonuniformity of these glasses is due to the particulars of the interaction between the structural elements (the interaction between SE of the same kind is much stronger than that between SE of different kinds), it can be shown [2] that the glass density ρ can be represented as

$$\rho = \rho_1 + \frac{(\rho_2 - \rho_1)x}{k(x_1 - x) + x}, \qquad (1)$$

where $k = V_1/V_2$ is the ratio of the molar volumes of the corresponding structural elements, while ρ_1 and ρ_2 are the densities corresponding to the structural elements SE1 and SE2. The expression (1) can be put into the form [1]

$$\rho = ax^2 + bx + c, \qquad (2)$$

where a, b, and c contain the same parameters of the SE but here we shall employ the initial expression (1).

It follows from the dependence of the relative change of the density on the pressure dp under hydrostatic compression

$$\frac{d\rho}{\rho} = \frac{dp}{K} \qquad (3)$$

that the bulk modulus K can be related with the density. Indeed, considering ρ and $k(\rho)$ to be functions of p, we shall

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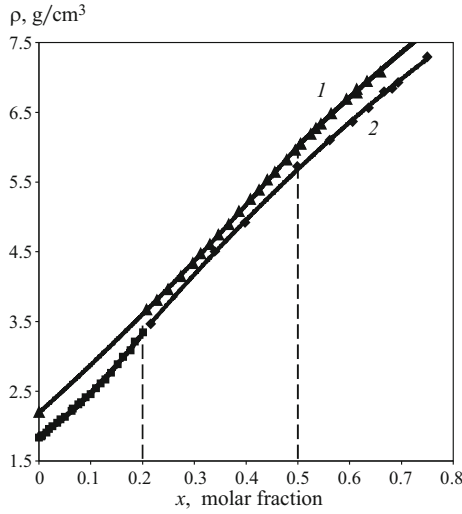[1] Moscow State Night Metallurgical Institute, Moscow, Russia (e-mail: samovv@mail.ru).

Fig. 1. Glass density versus the modifier PbO content: *1*) PbO–SiO$_2$, L. I. Demkina's data presented in [3]; *2*) PbO–B$_2$O$_3$: $x < 0.2$, data of R. R. Shaw and D. R. Uhlman presented in [5]; $x > 0.2$, M. S. Heinrich's data presented in [4].

show using the expression (1) that the density change accompanying a pressure change is

$$d\rho = d\rho_1 + \frac{(d\rho_2 - d\rho_1)x}{k(x_1 - x) + x} - \frac{(\rho_2 - \rho_1)(x_1 - x)x}{[k(x_1 - x) + x]^2}. \quad (4)$$

Introducing the variable $\rho = \rho/K$, we obtain

$$\left.\begin{array}{l} d\rho = \gamma dP; \\[4pt] \dfrac{x}{k(x_1 - x) + x} = \dfrac{\rho - \rho_1}{\rho_2 - \rho_1}; \\[8pt] \dfrac{k(x_1 - x)}{k(x_1 - x) + x} = \dfrac{\rho_2 - \rho}{\rho_2 - \rho_1}; \\[10pt] dk = k\left(\dfrac{d\rho_2}{\rho_2} - \dfrac{d\rho_1}{\rho_1}\right), \end{array}\right\} \quad (5)$$

and using the relations (3) and (5) we write instead of (4)

$$\gamma = \gamma_1 + \frac{\rho - \rho_1}{\rho_2 - \rho_1}\left[\gamma_2 - \gamma_1 + (\rho_2 - \rho)\left(\frac{1}{K_1} - \frac{1}{K_2}\right)\right], \quad (6)$$

where γ_1, γ_2 and K_1, K_2 are the values of the corresponding quantities at the limits of the composition range of nonuniform structures.

Since the compositions at these limits are uniform and correspond to the structural elements SE1 at $x = 0$ and SE2 at $x = x_1$, no errors arise on averaging over the sound propagation velocities in a nonuniform medium.

Thus, knowing the characteristics of the nonuniform compositions at the range limits they can be calculated for any composition inside the range.

For two-component glasses with a uniform structure it is convenient to use the expression (2) in which

$$c = \rho_1;$$
$$b = (\rho_2 - \rho_1) + \rho_{12};$$
$$a = -\rho_{12}.$$

Here, the initial components can play the role of the SE. Since the properties of each component change when the components interact with one another, in the linear approximation of the dependence of the properties of one component on the content of the other component the parabolic dependence (2) is obtained for the density. In this case the structural elements SE1 and SE2 interact, forming a phase with variable composition, and ρ_{12} is an indicator of the interaction between the structural elements SE1 and SE2. Assuming the compositions of the SE coincide with the components, x is the SE2 fraction in the solid solution SE1 + SE2.

In contrast to glasses with a nonuniform structure, the concept of local density is introduced for the glasses being studied here: ρ_i — when a SE is surrounded by SE which are similar to it and ρ_i' — when a SE is surrounded by elements of a different kind. As a result

$$\rho_{12} = \rho_1' - \rho_1 + \rho_2' - \rho_2 = \Delta\rho_1 + \Delta\rho_2. \quad (7)$$

Having tied the density change $d\rho$ to the pressure increment dp, we obtain the function $\gamma(x)$

$$\gamma = a_\gamma x^2 + b_\gamma x + c_\gamma, \quad (8)$$

where

$$\left.\begin{array}{l} a_\gamma = -\left(\dfrac{d\rho_2}{\rho_2} - \dfrac{d\rho_1}{\rho_1}\right); \\[10pt] b_\gamma = \gamma_2 - \gamma_1 - a_\gamma; \\[6pt] c_\gamma = \gamma_1, \end{array}\right\}$$

and γ_1, γ_2 and K_1, K_2 are the values of γ and K for the corresponding structural elements of the glasses. In the case at hand such SE are the oxides of silicon and lead for the lead-silicate glasses and the oxides of boron and lead for lead-borate glasses.

Thus, in the composition range of uniform structure ($x_1 \le x \le 1$) the dependence $\gamma(x)$, just as $\rho(x)$, is parabolic.

As an example of the application of the method, we shall consider lead-silicate and lead-borate glasses. It follows from the form of the composition dependence of the density of these glasses (Fig. 1 — sections of the computed curves with positive curvature) that in some content range for the modifier PbO ($0 \le x \le x_1$) the structure of these glasses is heterogeneous; for silicate glasses $x_1 = 0.5$ molar fractions while for borate glasses $x_1 = 0.2$ molar fractions. The data for the modulus K and the computed curves for these glasses are

presented in Fig. 2. The values of the computed parameters are indicated in Table 1.

Handbook data for quartz, lead-silicate, and lead-borate glasses were used for the calculations [3, 4]. Preference was given to works where the density and elastic characteristics were determined for one and the same samples. Comparing the figures shows that the spread of the experimental points in determining the density is much smaller than in determining the bulk modulus.

The parameters of the computed functions $\rho(x)$ and $K(x)$ in the composition range $x \le x_1$ were determined using the experimental values of $\rho_1 = \rho(0)$, $K_1 = K(0)$, $\rho_2 = \rho(x_1)$, $K_2 = K(x_1)$ and the computed values of $k = V_1/V_2$, where $k = 1.26$ for lead-borate glass and $k = 1.17$ for lead-silicate glass. Next, the relation (6) was used to calculate $\gamma = \gamma(\rho)$ and $K(\rho) = \rho/\gamma$.

The function $\gamma(x)$ following the parabolic law (8) in the composition range $x > x_1$ was determined from the experimental data on $K(x)$ for lead-borate glasses and the computed values of $\rho(x)$. This made it possible extrapolate $\gamma(x)$ to the entire composition range $x_1 < x < 1$ and then compute the function $K(x) = \rho(x)/\gamma(x)$.

For lead-borate glasses, the individual computed curves in the composition range with homogeneous and heterogeneous structure are in quite good agreement with the experimental points but do not match with one another near $x = x_1$. This can be explained by the fact that in the composition range near a boundary separating glass with homogeneous and heterogeneous structure there is also no linking between the experimental data (they were obtained by different authors and by different methods: R. Shaw and D. Uhlman used echo pulses, A. Osaka and colleagues used the pulse superposition method), while the computed curves are constructed directly from the experimental data.

For lead-silicate glasses, the data on the elastic properties in the composition range for homogeneous structure are inadequate to establish from them the dependence $\gamma(x)$, while for glasses with nonuniform structure the results of B. I. Kisin and I. N. Korolenko from S. V. Nemilov's work, which are presented in [4], are characterized by a small spread. These data were used to determine the parameters of the curve for $x < x_1$. The parameters of the curve $\gamma(x)$ for the composition range $x > x_1$ were calculated according to the values of $\gamma(0)$ and $\gamma(0.5)$ for lead-silicate and $\gamma(1)$ for lead-borate glasses, i.e., the calculation of these parameters is in no way related with existing experimental data (only two points) and is based on the suppositions that the properties of SE2 for $x = 1$ are the same for lead-borate and lead-silicate glasses, SE1 is common to both glasses with homogeneous and heterogeneous structure,
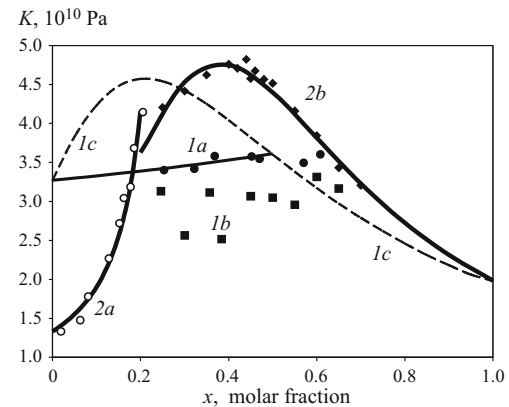

Fig. 2. Bulk modulus K versus the content x of the modifier PbO: *1*) PbO–SiO$_2$: *1a*) [4] (S. V. Nemilov cites measurements performed by B. I. Kisin and I. N. Korolenko); *1b*) measurements performed R. R. Shaw and D. R. Uhlman, presented in [3]; *1c*) curve computed according to the values of K at the points $x = 0$, $x = 0.5$, and $x = 1$; *2*) PbO–B$_2$O$_3$: *2a*) $x < 0.2$ according to data of R. R. Shaw and D. R. Uhlman, presented in [3]; *2b*) $x > 0.2$, according to data obtained by A. Osaka, N. Soga, and M. Kunuji, presented in [4].

while the elastic properties of glasses from both ranges are the same at $x = 0.5$.

Figure 2 displays the computed curves for two types of glasses with different glass formers and the same modifying agent.

The calculation of the curve *1c* relied on the data for pure silica and lead oxide as well as on the extrapolation of the computed curve *1a* to the composition $x = 0.5$. The data for lead oxide were obtained by extrapolating the curve *2b* to $x = 1$. Figure 2 also displays the experimental points, obtained by R. Shaw and D. Uhlman and published in the handbook [3], which are not taken into account at all and only demonstrate the spread of the data obtained by different authors (curve *1a* and points *1b*).

Thus, the satisfactory agreement between the computed curves and the experimental points in the composition range for nonuniform structure indicates that the average size of the nonuniformities $\delta \ll \lambda \approx 100$ μm. On the other hand, for

TABLE 1. Values of the Computed Parameters

Glass	x_1, molar fractions	ρ_1, g/cm^3	ρ_2, g/cm^3	ρ_{12}, g/cm^3	$K_1 \times 10^{-10}$, Pa	$K_2 \times 10^{-10}$, Pa	$a_\gamma \times 10^{10}$, g/(cm$^3 \cdot$ Pa)
PbO–SiO$_2$	0.5	2.2	6.05	–	3.28	3.61	–
	0.5	2.2	9.01	2.43	3.28	1.96	3.7
PbO–B$_2$O$_3$	0.2	1.84	3.35	–	1.33	4.15	–
	0.2	1.84	8.95	0.93	1.33	1.98	6.66

Note. The numerator and denominator refer to glasses with heterogeneous and homogeneous structure structures, respectively. However, for the glasses PbO–SiO$_2$, $\rho_2 = 6.05$ g/cm^3 and $K_2 = 3.61 \times 10^{10}$ Pa are the density and modulus K of the glass at the heterogeneous structure limit, i.e., $x = x_1 = 0.5$ molar fractions.

this spread of the measurements of the elastic properties obtained by different authors by different methods, the method proposed here cannot be used as a theoretical method of calculating these characteristics, because it depends on the results of the measurements. But the theoretical curves $\gamma(\rho)$ obtained for homogeneous and $\gamma(x)$ for heterogeneous glass composition ranges give a rational method of "smoothing" the existing experimental results.

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